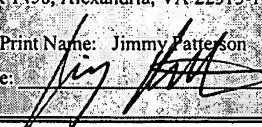


**APPLICATION
FOR
U.S. PATENT**

TITLE: Pre-treatment of Hydrocarbon Feed Prior to Oxidative Desulfurization

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**PRE-TREATMENT OF HYDROCARBON FEED PRIOR TO OXIDATIVE
DESULFURIZATION**

PRIOR RELATED APPLICATIONS

[1] Not applicable.

5 FEDERALLY SPONSORED RESEARCH STATEMENT

[2] Not applicable.

REFERENCE TO MICROFICHE APPENDIX

[3] Not applicable.

FIELD OF THE INVENTION

10 [4] The invention relates to removing polyene compounds from hydrocarbon streams which are detrimental to further refinery processing, especially desulfurization via oxidation.

BACKGROUND OF THE INVENTION

15 [5] Fluid catalytic cracker (FCC) gasoline and gasoline blends containing FCC gasoline, which has not been hydrotreated, contain highly unstable, reactive toward oxidation and polymerization, polyenes, such as dienes and styrenes, in addition to mono-olefins. Typically the amount of these compounds in the petroleum hydrocarbon streams of interest is in the range of from about 0.5 to about 10 % wt. These streams also contain a variety of sulfur compounds, as well as nitrogen compounds in a wide range of concentrations, e.g. from 15 ppm to 4000 ppm sulfur. Also, current commercial diesel fuel may be blended with Light Cycle Oil (LCO), which may not have been hydrotreated, and as a result the blend contains cracked, reactive hydrocarbons, which are reactive toward oxidation and polymerization.

20 [6] In recent years there have been a number of processes proposed, and some of them developed and demonstrated to desulfurize petroleum hydrocarbon streams, including gasoline and diesel, via an oxidative route. A number of oxidants, such as hydrogen peroxide

with carboxylic acids, carboxylic peracids, hydro peroxides (e.g. tertiary butyl hydro peroxide), ozone, oxygen, etc. have been shown to oxidize a wide range of sulfur species in liquid petroleum hydrocarbons to, e.g. sulfones, sulfoxides, sulfonic acids and the like. These reaction products are more polar and boil at higher temperatures than their respective precursors, thus
5 enabling selective removal from the host hydrocarbon matrix, resulting in a desulfurized liquid hydrocarbon product. The selective removal of the oxidized sulfur compounds from their host matrix can be achieved by liquid-liquid solvent extraction with polar solvents, adsorption on solids, such as alumina, silicates, etc., or by distillation. The separation process depends on the composition and physical properties of the feed hydrocarbon stream.

10 [7] Oxidant consumption is very large when desulfurization is applied to feeds containing large amounts of cracked, unstable compounds. These compounds compete strongly with the sulfur compounds for the oxidant; i.e. little sulfur oxidation takes place until almost all of the polyenes (e.g. dienes) react with the oxidant. The oxidant is expensive and process economics suffer if excess oxidant is necessary for feeds containing very large amounts of
15 dienes, e.g. 10,000 ppm (i.e. 1 wt%) relative to sulfur, e.g. 320 ppm. To oxidize sulfur, the stoichiometric requirement of hydrogen peroxide is 2 moles peroxide per mole sulfur. To oxidize dienes, the stoichiometric requirement is 1 mole peroxide per mole diene. For a typical diene with a rounded up molecular weight of 100, and for the above exemplary feed, the requirements are $(10000/100)/2 = 50$ for dienes relative to $320/32 = 10$ for sulfur, and their ratio
20 would be $50/10 = 5$, meaning 5 times more peroxide is needed to satisfy the dienes, before the oxidation of sulfur can take place effectively.

[8] Therefore, a method is needed to react polyene compounds and other reactive hydrocarbons from petroleum streams before desulfurization processes, particularly oxidative desulfurization.

25

SUMMARY OF THE INVENTION

[9] The above need is met by a process for selectively reacting polyene compounds which hinder oxidative desulfurization, such as dienes from a hydrocarbon stream. The process comprises contacting and mixing with the liquid hydrocarbon stream containing polyene compounds sulfuric acid, in an amount from about 0.5 to about 10 vol % based upon the

hydrocarbon stream to convert the polyunsaturated olefin compounds (polyenes) present to saturated compounds. The reaction results in a hydrocarbon phase with substantially no loss in octane number and an aqueous spent acid phase. The phases are separated to recover the hydrocarbon product for further treatment to remove the sulfur. The sulfuric acid may be 5 recycled effectively by adding a small amount of fresh acid.

BRIEF DESCRIPTION OF THE DRAWINGS

[10] FIG. 1 shows a schematic flow sheet of the preferred process of the instant invention wherein a lower product specification is desired.

[11] FIG. 2 shows a schematic flow sheet of the preferred process of the instant 10 invention wherein a higher product specification is desired.

[12] FIG. 3a is a GC/SCD chromatogram of Example 1 pre-oxidation.

[13] FIG. 3b is a GC/SCD chromatogram of Example 1 post-oxidation.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[14] The invention summarized above will be more completely described as set forth 15 hereinafter.

[15] Embodiments of the invention provide a process for selectively reacting polyenes from a hydrocarbon stream. The process comprises the steps of contacting the hydrocarbon stream containing polyenes with sulfuric acid at ambient temperature and for a time sufficient to form a hydrocarbon phase, with substantially no loss in octane or cetane number and an aqueous 20 spent acid phase. The hydrocarbon phase is then separated from the aqueous spent acid phase.

[16] The process of this invention selectively reacts polyene compounds when polishing fluid catalytic cracker (FCC) gasoline, gasoline blends containing FCC gasoline, commercial diesel fuel, straight run diesel and fuels containing light cycle oil (LCO) kerosene prior to oxidation desulfurization of the hydrocarbon fuel feed.

[17] In a preferred embodiment, referring to Fig. 1, a petroleum hydrocarbon feed 102 is sent to a polyene pre-treater 10, along with sulfuric acid 104. The pre-treater is preferably maintained at ambient temperatures and pressures, approximately from about 0 °C to about 60 °C and from about 10 to about 50 psi. The reactions are not affected by pressure, but some pressure is used to maintain the continuous process with a desired liquid flow. However, the reaction would work at various operating conditions found in refining industry processes. The reactions are exothermic and reactor temperature is cooled using equipment and processes known to those skilled in the art. The reaction occurs within 5 minutes or less. The feed is a typical petroleum hydrocarbon stream found in a typical refining environment that includes polyene compounds. Polyene compounds include compounds having two or more unsaturated sites, such as dienes and styrenes. The petroleum hydrocarbon streams include FCC gasoline, straight-run diesel, diesel, light cycle oil (LCO), commercial gasoline, and diesel that has LCO added to it. In a preferred embodiment the petroleum hydrocarbon stream is a FCC gasoline stream. The petroleum hydrocarbon stream typically has from about 0.5 to about 3 wt % of polyenes, typically 1 wt % and from about 50 to about 4000 ppm sulfur. The petroleum hydrocarbon stream may also contain nitrogen compounds in the range of from about 0 to 900 ppm.

[18] In a preferred embodiment, the polyene pre-treater 10 includes equipment for thoroughly contacting the petroleum hydrocarbon feed 102 and the sulfuric acid 104. This equipment may be a mixer, stirrer or any equipment known to those skilled in the art that contacts the petroleum hydrocarbon feed 102 and the sulfuric acid 104. Contacting in this specification is defined as ensuring that the petroleum hydrocarbon stream and the sulfuric acid 104 are in intimate contact so that the acid reacts with the unsaturated hydrocarbons to saturate them.

[19] The amount of sulfuric acid is from about 0.5 to about 10 vol% relative to the feed, preferably from about 1 to about 4 vol%, more preferably from about 2 to about 3 vol%. When sulfuric acid is used the strength of the acid is greater than about 80 % by weight, the preferred strength is from about 80 wt% to about 98 wt%, more preferably from about 89 wt% to about 93 wt%. In an especially preferred embodiment, the sulfuric acid strength is about 93 wt%, which is commercially available, non-corrosive and easy to handle. When operating the

process using 93 wt% sulfuric acid, the reaction proceeds without having to be cooled. If 98 wt% sulfuric acid is used, cooling of the reaction is necessary to prevent oxidation of mono-olefins and a loss in the octane rating of the hydrocarbon phase. The amount of acid is also dependent on the amount of polyenes in the feed. In a preferred embodiment, the polyenes are 5 dienes which react to produce compounds that are not reactive with peroxides. If sulfuric acid is used, sulfates are produced. If excess amounts of acid are added and temperatures above ambient (from about 25 to about 60 °C) are used, reactions may occur with other feed components possibly reducing the octane and the hydrocarbon yield. Mono-olefins remain substantially unchanged keeping octane levels substantially equal. In a preferred embodiment, 10 sufficient acid is added to the hydrocarbon feed to form two phases. By controlling the amount and strength of sulfuric acid, contact time, and temperature, the octane level of the hydrocarbon phase remains substantially unchanged and the polyenes are reacted.

[20] In a preferred embodiment, the sulfuric acid 104 may be any spent sulfuric acid stream found in a refinery or chemical plant. In particular, the spent sulfuric acid from a sulfuric acid alkylation process may be used. The strength of the useful spent alkylation sulfuric acid ranges from about 85 wt% to about 93 wt%. In a preferred embodiment, the spent alkylation sulfuric acid is about 90 wt %, in an amount that is 1 to 3 wt% relative to the hydrocarbon feed with a contact time from about 2 to about 5 minutes at a temperature of from about 40 °C to about 50 °C.

20 [21] The reaction product 106 between the acid and the petroleum feed is fed to a separation/washing section 20. The reaction product separates into two phases, an oil phase and an aqueous spent acid phase. The oil phase is separated and washed with water 108 to remove residual acid and produce a treated oil phase 110. The treated oil phase 110 is then sent to a desulfurization operation 30. Equipment in the separation/washing section 20 may include 25 liquid-liquid extractors, coalescers, and the like.

[22] By using sulfuric acid, the treated oil phase 110 when analyzed may show an increase in total sulfur, sometimes as much as 2-8 times more than the feed 102. This occurs because the sulfuric acid reacts with the polyenes to form sulfates. The sulfuric acid also reacts with other sulfur compounds, i.e., mercaptans, sulfides in the feed 102 to form a variety of

disulfide compounds. These disulfides may be partially extracted into the spent acid phase 112, but a relatively large proportion of the sulfates also remain in the treated oil phase. The net effect of these reactions is an increase in the total sulfur in the treated oil phase 110 and a decrease of the original sulfur that remains to be oxidized in a subsequent step to enable a 5 desulfurized final product. During oxidation, the remaining portion of the original sulfur compounds, i.e., thiophenes and benzothiophenes, along with the disulfides in the oil phase are oxidized to the corresponding sulfones, sulfoxides, and sulfonic acids. A large amount of these sulfur compounds are extracted into the aqueous spent acid of the oxidation solution. The sulfur in the form of sulfates, does not compete for oxygen but may undergo a hydrolysis reaction 10 which is slower relative to the other sulfur oxidation reactions. The net result, after several stages of oxidation, is the total sulfur decreases after each stage but may still be higher than the original total sulfur, when the feed is gasoline. The sulfates formed by the saturation of polyenes are stable in their high oxidation state with a boiling point greater than the 95% hydrocarbon range (typically above 230 °C). Furthermore, by using the amount of acid in the ranges listed 15 above, significant amounts of low boiling point organic sulfur species are reacted to form high boiling point organic sulfur species, part of which extract into the acid phase and part of which remain in the oil phase. As a result of these reactions and partial extraction in the acid phase, there is a net reduction in the amount of sulfur to be oxidized and removed by subsequent processes in the gasoline or diesel boiling ranges, dependent on the feed creating a reduction in 20 oxidant consumed.

[23] The spent acid 112 can be reused multiple times and therefore is preferably recycled to the pre-treater 10. As the effective strength of the acid decreases, incremental amounts of fresh acid are added to the spent acid to restore activity. Incremental amounts of sulfuric acid are those amounts that are added to the recycle spent acid stream 112 to restore the 25 strength of the acid and the volume ratio after bleeding a portion of the spent acid stream 112. The spent acid phase 112 contains miscellaneous organics and some sulfur compounds. Sulfur compounds which react with sulfuric acid, especially mercaptans, sulfides and to some extent thiophenes are extracted into the spent acid phase 112 along with some basic nitrogen compounds which were also reacted. The generated sulfates in the spent acid phase 112 may be 30 hydrolyzed removing sulfates and recovering hydrocarbons as alcohols.

[24] Dienes are reacted to eliminate them from the competition with sulfur for oxygen, thus making the oxidation practical and economically viable (peroxide consumption is minimized). At the same time, sulfuric acid reacts with some of the sulfur species, e.g. mercaptans, sulfides and thiophenes, and partially extracts them into the spent sulfuric acid. As a 5 result, the amount of remaining original sulfur compounds in the gasoline boiling range that still need to be oxidized is lower, reducing the amount of peroxide needed for oxidation. The sulfates in the oil phase (which increases the total sulfur content) are stable against oxidation at the conditions of the oxidation process.

[25] The desulfurization operation 30 may be any process known to remove sulfur 10 from a petroleum hydrocarbon stream such as oxidation or hydrotreating, for example. These operations include oxidative desulfurization. Oxidative desulfurization processes are those in which mixtures of hydrogen peroxide and carboxylic acids (such as formic or acetic acid), ozone, peracids (such as formic or acetic peracids), or hydroperoxides (such as tertiary butyl hydro peroxide) are reacted with the sulfur compounds in a petroleum hydrocarbon stream. In a 15 preferred embodiment, an oxidative desulfurization process is used such as those described in U.S. Patent Nos. 6,402,940 and 6,406,616 which are hereby incorporated by reference in their entirety. Those patents disclose an oxidative desulfurization process using dilute hydrogen peroxide and formic acid as the aqueous oxidant.

[26] The oxidative desulfurization process economically reduces the sulfur content to 20 an amount of from about 5 to about 15 ppm for diesel, and from 8-30 ppm for gasoline, in some instances even less and does not substantially diminish the cetane or octane rating of the treated oil phase 110. The treated oil phase 110 contains substantially lower amounts of the original organic sulfur compounds in the feed, i.e., up to about 1500 ppm, but higher amounts of total sulfur due to sulfates formed in the reactions described above. The treated oil phase 110 is 25 contacted with an oxidizing solution containing hydrogen peroxide, formic acid, and a maximum of about 25 percent water including the water in the peroxide and formic acid solution. The amount of the hydrogen peroxide in the oxidizing solution is greater than about two times the stoichiometric amount of peroxide necessary to react with the sulfur in the treated oil phase 110, not including the sulfur in the generated sulfates. By effectively removing the interference of 30 polyenes to sulfur oxidation, the amount of oxidizing solution is optimized to only that amount

necessary to remove the sulfur components that are reactive to the oxidizing solution. The oxidizing solution contains hydrogen peroxide at low concentration, the concentration, in its broadest sense, from about 0.5 wt % to about 4 wt %. The oxidation reaction is carried out at a temperature ranging from about 50 °C to about 130 °C, a pressure ranging from about 15 psi to 5 about 250 psi, for less than about 15 minutes contact time at optimum conditions. The total pressure of the reaction will be dependent upon the partial vapor pressures of the treated oil phase 110, formic acid, hydrogen peroxide, and water at the selected operating temperature, plus additional pressure from any additional inert gas used. The oxidizing solution has, not only a low amount of water, but small amounts of hydrogen peroxide with the formic acid being the largest 10 constituent. Two phases are formed, a hydrocarbon phase and an aqueous phase. Some of the oxidation products, usually the corresponding organic sulfones, become soluble in the oxidizing solution and, therefore, are removed from the oxidized fuel by a subsequent phase separation step. The aqueous phase is removed from the hydrocarbon phase.

[27] For diesel feed, after separation, the hydrocarbon phase may be water washed and 15 passed through a salt dehydrator, or contacted with a caustic solution, washed and passed through a salt dehydrator, or contacted with anhydrous calcium oxide (i.e., quicklime) and/or passed through filtering devices to neutralize any trace acid remaining and to dehydrate the hydrocarbon fuel 114. In an alternate embodiment, the hydrocarbon fuel is further passed over a suitable solid adsorber, such as solid alumina, silica gel, or aluminosilicates, at temperatures up 20 to 110 °C, to adsorb the residual oxidized sulfur compounds soluble in the hydrocarbon fuel, if any are present. The hydrocarbon fuel product is now substantially desulfurized, neutralized, and dry.

[28] In a preferred embodiment for gasoline feed, the hydrocarbon fuel 114 is sent to a distillation column 40 to produce a primary hydrocarbon product 116 that meets product 25 specifications for low sulfur; and a secondary hydrocarbon product 118 containing unwanted sulfur components. The shifting of some sulfur compounds to a higher boiling point, in the pre-treater 10, makes distillation of the hydrocarbon fuel 114 possible to remove sulfur products from the hydrocarbon fuel to produce the primary hydrocarbon product 116 having very low hydrocarbon yield loss and substantially no octane loss. Preferably, the primary hydrocarbon 30 product 116 is further water washed to further reduce its sulfur content to lower values and

dehydrated to yield the final product. The secondary hydrocarbon product 118 can be recycled into other refinery processes units or blended into other high sulfur products. Preferably, a suitable higher boiling hydrocarbon stream is fed into the distillation column 40 to act as a heel for the distillation and will exit with the secondary product 118. The ratio of this heel 5 hydrocarbon stream to stream 114 can be adjusted in a typical range from about 1 to about 10 wt%, preferably from about 1 to about 5 wt% of the hydrocarbon stream charged to the distillation column 40.

[29] It is a feature of the invention that product recovered in the treated oil phase 110 goes through the desulfurization oxidation process 30 while leaving undisturbed the carbon to 10 hydrogen ratio and the olefinic compounds which contribute to either the octane or cetane rating of the hydrocarbon fuel, gasoline or diesel. Octane rating is the resistance of the hydrocarbon fuel to burn. The higher the rating, the slower the burn when ignited during the compression burn cycle of the piston. Higher octane allows for better control of burning for high compression engines.

[30] Within the desulfurization process 30, the oxidized sulfur compounds are separated from the hydrocarbon phase 114, or raffinate, and treated to recover the formic acid for recycle. The separation between the hydrocarbon phase and the aqueous phase can be accomplished in a number of ways, but the preferred separation occurs by the use of a liquid- 15 liquid separator operated at a temperature sufficiently high, close to the oxidation reaction temperature, to result in gravity separation of the material. The aqueous phase, of course, being heavier than the hydrocarbon phase would be drained from the bottom of the separation device where it may be preferably mixed with a suitable high boiling range refinery stream, such as for example, a light gas oil, and flash distilled to remove the water and acid overhead while transferring and leaving the sulfur-containing compounds in the gasoil stream exiting at the 20 bottom of the distillation column. The overhead stream containing acid and water from the flash distillation tower is further distilled in a separate column to remove a portion of its water for disposal. The acid recovered can then be returned to the oxidizing solution make up tank where it is combined with the hydrogen peroxide to form the oxidizing solution and again contact the sulfur-containing fuel feed. This preservation of the carboxylic acid enhances the economics of 25 the desulfurization process. The optimization of the oxidizing solution also results in savings 30

relating to the formic acid regeneration and make-up since the peroxide to formic acid ratio is fixed within a narrow, workable range.

[31] The oxidizing solution of the desulfurization process 30 is preferably formed by mixing a commercially-available 96-99 wt%, by weight, formic acid solution, preferably regenerated and recycled as described above, with a commercially-available hydrogen peroxide solution normally the 30 wt%, 35 wt% and 50 wt% concentration commercially available in order to avoid the dangers connected with handling a 70 wt% hydrogen peroxide solution in a refinery environment. A full description of the oxidizing solution and process is disclosed in U.S. Patent Nos. 6,402,940 and 6,406,616 which are hereby incorporated by reference in their entirety. The resulting oxidizing solution contains from about 0.5 wt% to about 4 wt% hydrogen peroxide, less than 25 wt% water with the balance being formic acid. The water in the oxidizer/extractor solution normally comes from two sources, the peroxide and acid solutions used, and the recycled formic acid which includes part of the water formed in the oxidation reaction, when the process operates in the recycle mode. On occasion, additional water could be added without being detrimental to the practice of this invention as long as the criteria explained herein are considered, but it is important to an economical process to keep the water content low as set forth herein. The preferable concentration of hydrogen peroxide in the oxidizer solution, which is consumed in the reaction, would be from about 1% to about 3% by weight, and most preferably from about 2 wt% to about 3 wt%. The water content would be limited to less than about 25 wt%, but preferably between about 8 wt% and about 20 wt%, and most preferably from about 8 wt% to about 14 wt%. The oxidation/extraction solution used in the practice of this invention will contain from about 75 wt% to about 92 wt% of carboxylic acid, preferably formic acid, and preferably about 79 wt% to about 90 %wt formic acid. The molar ratio of acid, preferably formic acid, to hydrogen peroxide useful in the practice of this invention is at least about 11 to 1 and from about 12 to 1 to about 70 to 1 in the broad sense, preferably from about 20 to 1 to about 60 to 1.

[32] The oxidation solution accomplishes a rapid and substantially complete oxidation of the sulfur compounds, and their substantial extraction from such refined products as diesel fuel, jet fuel, or gasoline, whether motor, racing or aviation gasoline, which contain from about 30 to about 1500 ppm sulfur and will perform effectively to oxidize and extract organic sulfur

present in fuels at greater concentrations. Since the moles of hydrogen peroxide to be used is proportional to the amount of sulfur present and since the peroxide is consumed, the cost of this material can have a negative effect on the economics of the operation if the amount of sulfur present is high. Therefore, the desulfurization process 30 is most useful for polishing small amounts of sulfur, such as for example less than about 1500 ppm from hydrocarbon fuels ready for market than for removal of sulfur from crude oil containing gross amounts of sulfur.

[33] In the oxidation of organic sulfur compounds using hydrogen peroxide, the stoichiometric reaction ratio is two moles of the hydrogen peroxide consumed per mole of sulfur reacted. The amount of oxidizing solution used should be such that it contains at least about two times the stoichiometric amount to react the sulfur present in the fuel, preferably from about two to about four times. Greater amounts could be used, but only at increased cost since it has been found that improvement of sulfur oxidation is marginal at best when the amount is greater than four times the amount needed. Furthermore, to minimize peroxide losses by decomposition side reactions, the hydrogen peroxide concentrations in the oxidizer composition of this invention are preferably adjusted at low levels about 0.5 wt % to about 4 wt %. At these levels and the reaction temperature of about 85-95 °C and a pressure of about 15 to about 250 psi, depending upon the hydrocarbon involved it has been discovered that the rapid and complete oxidation, and extraction, of the sulfur compounds from hydrocarbon feeds of relatively low sulfur content, compete favorably with the side reaction of peroxide decomposition, resulting in a practical and economic process for desulfurization of such fuels.

[34] More specifically for gasoline feeds, it is theorized that during distillation, the sulfates generated by the sulfuric acid pre-treatment partially thermally decompose to yield sulfur trioxide (SO₃) and sulfur dioxide (SO₂). The oxides exit with the primary hydrocarbon product 116 and increase its total sulfur content which may be attributable to solubility in the oil phase. Removal of these oxides from the overhead product can be by either 1) water washing, or 2) by mixing with anhydrous lime (slurry) followed by separation (settling/thickening and/or filtration). Lime (i.e., quicklime, CaO) is used to neutralize and dehydrate both the hydrocarbon fuel 114 fed to the distillation column 40, and the primary hydrocarbon product 116. The result is the stable hydrocarbon fuel product 120 has a minimum residual sulfur content. As an added feature, by neutralizing and dehydrating the hydrocarbon fuel 114, the possibility of corrosion is

minimized in the distillation column 40. The primary hydrocarbon product 116 is contacted with the lime in a mixer and transferred to a settler. The hydrocarbon fuel product 120 is passed through a filter before storage. The used lime and the lime cake from the filter is sent to contact the hydrocarbon fuel 114 in a mixer/filter before entering the distillation column 40. The 5 advantage of lime versus water washings include the elimination of sludge formation during water washing and aqueous neutralization and the elimination of hydrocarbon losses in the waste water. The hydrocarbon in the exiting hydrocarbon-wet filter cake is recovered and recycled by passing the wet cake through a conventional low temperature thermal dryer. The dried used lime is partially hydrated, and contains some calcium sulfate and sulfite. The dried used lime can be 10 partially recycled to the process 50 with the addition of fresh make-up lime. The amount of lime added in the process is in excess of that required to dehydrate and neutralize the hydrocarbon fuel 114 and the primary hydrocarbon product 116. In an alternate embodiment, before neutralization the primary hydrocarbon product 116 is sent to a coalescer to remove the bulk of the discrete acid phase.

15 [35] Referring to Fig. 2, in an alternate embodiment, the feed 102 may have increased sulfur and a wider sulfur speciation, such as in diesel fuel. Therefore, the primary hydrocarbon product 116 may contain additional sulfur components after the reaction which are removed by selected solid adsorbants such as, for example, in a cyclic adsorption-desorption operation 50 to achieve a substantially sulfur-free hydrocarbon fuel product 120. The adsorption-desorption 20 operation also recovers the sulfur compounds in a concentrated form, practical for their final, environmentally benign, disposition within a refinery.

[36] In an alternate embodiment, the desulfurization process 30 is a hydrotreater. The hydrotreater selectively reduces and reacts sulfur compounds. Hydrotreating processes, catalysts and conditions are known and practiced in the art.

25 [37] In an alternate embodiment, the feed 102 is first sent to a mild hydrotreater. The hydrotreater selectively saturates the dienes and other reactive cracked compounds along with removing some sulfur and nitrogen compounds. Such hydrotreating processes are known and practiced in the art. Catalysts with low activity and selectivity only for very reactive, unstable,

polyunsaturated compounds are used. Such very mild, selective hydrotreating processes are known and practiced in the art.

[38] The foregoing described invention is further demonstrated by the following examples, which are offered for purposes of illustration of the practice of this invention and for 5 the understanding; not for the limitation thereof.

EXAMPLE 1

[39] To demonstrate existing oxidation desulfurization processes, a synthetic heavy naphtha was prepared by mixing the various components as shown in Table 1. The synthetic heavy naphtha contained no dienes, only olefins as unsaturates. A 250 ml sample of synthetic 10 naphtha containing 202 ppm S was oxidized by adding an oxidizing solution containing 1.714 ml of 35 wt% hydrogen peroxide and 50.5 ml formic acid 96 wt%. The mixture of naphtha and oxidizing solution was placed in an autoclave at 90 °C and stirred for 30 minutes. 20 psi of Argon is added at ambient temperature to the autoclave and the mixture is normally maintained 15 at about 40 to about 60 psi, but is dependent on the boiling range of the feed. After analysis, the oxidative desulfurization essentially removed 90% of the total sulfur. Figure 3a shows a GC/SCD chromatogram of the sulfur content of the initial feed containing 202 PPM S. Figure 3b shows a GC/SCD chromatogram of the product after the oxidation reaction having a total sulfur content of 18 PPM. The 18 PPM of sulfur were split into 9 PPM of non oxidized sulfur 20 compounds and 9 PPM of oxidized sulfur compounds. Little or no further sulfur separation was necessary since the oxidized sulfur compounds were removed fairly easily using alumina and the product had 9 PPM sulfur which is quite low. The hydrocarbon content, including the 1-decene, was unchanged.

Table I Model Synthetic Naphtha

Compounds	g	MW, g/n	n	ppm, S	density, g/ml
2,5-Me ₂ Thiophene	0.12	112.19	0.001	44	
Dipropylsulfide	0.16	118.24	0.001	57	
1-decene	78.57	140.27	0.560	0	
Heptyl Mercaptan	0.11	132.27	0.001	37	
n butylbenzene	156.01	134.22	1.162	0	
dodecane	511.81	170.34	3.005	0	
benzothiophene	0.12	184.26	0.001	28	
Totals	747.01			202	0.777
Actual measurement				202	0.777

EXAMPLE 2

[40] To demonstrate the effect of the presence of dienes during oxidation of 5 hydrocarbon feed containing dienes, a synthetic heavy naphtha was prepared by mixing the various components as shown in Table II. A 200 ml sample of the synthetic naphtha containing 202 ppm S with a half of a percent of both 2,5-dimethyl-2,4-hexadiene and 2,4-dimethyl-1,3-pentadiene was oxidized in an autoclave at 90 °C under 20 psi of Argon and the mixture is normally maintained at about 40 to about 60 psi, but is dependent on the boiling range of the 10 feed. The mixture is stirred for 30 minutes in three stages. The naphtha phase was separated and reoxidized two additional times. The aqueous oxidant per each stage was a mixture of 1.371 ml hydrogen peroxide (35%) and 40.4 ml formic acid (96%). During stage 1, essentially all of the heptyl mercaptan and dipropyl sulfide were reacted along with a substantial amount of the pentadiene. The 2,5-dimethyl-2,4-hexadiene was reduced by approximately one half. The 15 remaining hydrocarbon compounds and sulfur compounds remained almost unchanged. During stage 2, a second addition of the oxidation solution was added to the product from stage 1 and stirred for 30 minutes in an autoclave at 90 °C. Sulfur oxidation took place more rapidly due to fewer dienes competing for the oxidation solution. Dimethyl thiophene was reduced from 44 to 37 PPM. Benzothiophene was reduced to 26 PPM and dibenzothiophene was reduced to 7 PPM. 20 Only trace levels of dienes remained. The decene levels were not changed. For stage 3, a third addition of the same amounts of oxidant was added to the product of stage 2 and stirred for 30

minutes in an autoclave at 90 °C. The product from stage 3 contained only 10 PPM dimethylthiophene. The decene, butylbenzene, and dodecane were unchanged. The total sulfur content in the product was 20 PPM. These results are summarized in Table IIIa and IIIb which are hydrocarbon and sulfur balances, respectively. The dienes competed with the sulfur compounds for the oxidant. The hydrocarbon content of the product remained substantially the same as in the feed, except for the removal of the dienes. All of the dienes reacted before desulfurization reactions proceeded.

Table II Model Synthetic Naphtha plus Dienes feed

Compounds	g	MW, g/n	n	ppm, S	density, g/ml
2,5 Me ₂ Thiophene	0.03	112.19	0.000	44	
Dipropylsulfide	0.04	118.24	0.000	57	
1-decene	20.82	140.27	0.148	0	
Heptyl Mercaptan	0.03	132.27	0.000	37	
n butylbenzene	41.35	134.22	0.308	0	
dodecane	135.66	170.34	0.796	0	
benzothiophene	0.03	134.20	0.000	35	
dibenzothiophene	0.03	184.26	0.000	28	
2,5-Me ₂ -2,4-hexadiene	1.1	110.20	0.010	0	
2,4-Me ₂ -1,3-pentadiene	1.0	96.17	0.010	0	
Totals	200.10			200	0.777
Actual measurement				202	0.777

Table IIIa Synthetic Heavy Naphtha with Dienes product**(Hydrocarbon Balance, percentage)**

Stage	2,5 dimethyl-1,3-pentadiene	2,5 dimethyl-2,4-hexadiene	1-Decene	Butyl benzene	Dodecane
feed	0.46	0.50	9.94	21.13	67.59
1 st	0.03	0.26	9.99	21.09	68.09
2 nd	0.02	0.02	10.00	21.24	68.03
3 rd	0.01		9.35	21.07	68.56

Table IIIb Synthetic Heavy Naphtha with Dienes product
(Sulfur Balance, ppm S)

Stage	Dimethyl thiophene	Dipropyl Sulfide	Heptyl mercaptan	Benzo-thiophene	Dibenzo-thiophene	Total Non-oxidized
feed	51	51	28	44	29	203
1st	44			34	23	101
2nd	37			26	7	70
3rd	10					10

EXAMPLE 3

5 [41] To demonstrate the effectiveness of the pre-treatment of dienes prior to oxidation, the naphthenic feed as used in Example 2 was pre-treated with sulfuric acid. The dosage and contact time of sulfuric acid were stepwise, thereby establishing conditions for selective removal of dienes in the presence of regular olefins. 200 ml synthetic heavy naphtha with 1 wt% added dienes (see Example 2) was contacted with 1 ml sulfuric acid (98 wt%) and stirred for 2 minutes
10 at atmospheric pressure at a temperature of 24 °C. The resulting mixture was analyzed, see Table IVa and IVb, line 2. The mixture was stirred for 5 additional minutes and re-analyzed, see Table IVa and IVb, line 3. Another 1 ml sulfuric acid (98 wt%) was added to the mixture, stirred for 2 minutes, and analyzed, see Table IVa and IVB, line 4. The pretreated feed was stirred for 5 additional minutes and re-analyzed, see Table IVa and IVB, line 5. The solution rested and two
15 phases formed, the treated feed and the spent sulfuric acid. The spent sulfuric acid was separated from the pretreated feed and discarded. Oxidation of the treated feed used a solution of 1.029 ml hydrogen peroxide (35%) and 14.9 ml formic acid (96%). The mixture was stirred at 90 °C for 30 minutes in an autoclave. From Table IVa (hydrocarbon balance), the dienes were effectively reacted during the reaction with sulfuric acid without altering the rest of the hydrocarbon
20 content. From Table IVb (sulfur balance), sulfur compounds react with the sulfuric acid to form higher boiling point sulfur compounds, see addition products (i.e., alkyl or aryl sulfates). Even after oxidation, the non-sulfurous hydrocarbon content was unaffected, see Table IVa, line 6. Since the hydrocarbon content was unchanged, the octane content remained the same.

Table IVa Synthetic Heavy Naphtha with Dienes And H₂S0₄ Treatment
(Hydrocarbon balance, percentage)

Stage	2,5 dimethyl-1,3-pentadiene	2,5 dimethyl-2,4-hexadiene	1-Decene	Butyl benzene	Dodecane
feed, 200 ml	0.46	0.50	9.94	21.13	67.59
+1ml H₂SO₄, 2 min		0.32	10.28	21.33	67.36
H₂SO₄ + 5 min		0.27	10.14	21.29	67.55
+1ml H₂SO₄, +2 min		0.04	10.08	21.45	67.55
H₂SO₄, + 5 min			9.88	21.39	67.77
Oxidation Rxn			9.36	21.29	67.99

[42] Along with the dienes, heptyl mercaptan, dipropyl sulfide and some of dimethyl thiophene were reacted in the reactions with sulfuric acid. These compounds reacted to form 5 addition products. These addition products shifted to a high boiling point range, which could be separated by distillation not affecting the oxidation reaction. After oxidation, only 4 PPM of benzothiophene remained in the gasoline boiling range, much lower than the regulated value. Well beyond the gasoline boiling range, 117 PPM of heavy sulfur compounds, probably sulfate addition products, were removed by distillation.

Table IVb Synthetic Heavy Naphtha with Dienes And H₂SO₄ Treatment

(Sulfur Balance, ppm S)

Stage	Dimethyl Thiophene	Dipropyl Sulfide	Heptyl mercaptan	Benzo-thiophene	Di benzo thiophene	Addition products	Total Non-oxidized
feed, 200 ml	51	51	28	44	29		203
+1ml H₂SO₄, 2 min	25	3	1	35	29	29	122
H₂SO₄ + 5 min	15	2		35	29	53	134
+1ml H₂SO₄, +2 min	1			25	29	44	99
H₂SO₄ + 5 min	1			25	29	105	160
OxidationRxn				4		117	121

EXAMPLE 4

[43] To demonstrate the effect of adding excessive amounts of sulfuric acid prior to oxidation, 100 ml of heavy synthetic naphtha containing 202 ppm sulfur plus 1 wt% dienes (see Example 2) was contacted with 1 ml (1 wt%) sulfuric acid (98 wt%). A separate sample 5 was contacted with 10 ml (10 wt%) sulfuric acid (98 wt%). The mixtures were stirred, separately, in an autoclave for 5 minutes at 24 °C. Two phases formed, an oil phase and an acid phase. Analysis of the oil phases, See Table V, showed the mono-olefinic content of the gasoline was substantially reduced when excess (10 wt%) sulfuric acid was used. By affecting the mono-olefinic content, the octane rating of the oil phase was reduced. 10 Furthermore, a small amount of high boiling sulfur additions products were formed.

Table V Synthetic Heavy Naphtha with Dienes And Excess H₂SO₄ Treatment**(Hydrocarbon balance, percentage)**

Stage	2,5 dimethyl-1,3-pentadiene	2,5 dimethyl-2,4-hexadiene	1-Decene	Butyl benzene	Dodecane	Addition Products
feed	0.5	0.5	9.9	21.3	67.6	0.0
1% H₂SO₄	0.0	0.0	9.9	21.4	67.8	
10% H₂SO₄	0.0	0.0	6.3	21.2	70.4	0.6

EXAMPLE 5

[44] To demonstrate oxidation without prior diene pre-treatment of a high diene feed, CAT gasoline containing approximately 12 wt% olefins was oxidatively reacted in two stages. The first stage had 260 ml CAT gasoline, containing 310 ppm sulfur, oxidized with 0.651 ml hydrogen peroxide (35 wt%) plus 10.6 ml formic acid (96 wt%) at 90 °C and stirred for 30 minutes in an autoclave. The second stage oxidized approximately 250 ml of 20 partially oxidized CAT Gasoline from stage 1 with 0.625 ml of hydrogen peroxide (35 wt%) and 10 ml of formic acid (96 wt%). This mixture was stirred for 30 minutes in a 90 °C autoclave. The final product contained 305 PPM sulfur, most of which not oxidized. Therefore, a feed having a large amount of dienes was not sufficiently desulfurized by the oxidizing solution because the dienes more readily reacted with the solution than the sulfur 25 compounds.

EXAMPLE 6

[45] To demonstrate the effectiveness of diene pre-treatment prior to oxidation of high diene feed, the CAT gasoline of Example 5 was pre-treated with sulfuric acid and oxidized. 250 ml of CAT Gasoline (310 ppm S) had 2.5 ml sulfuric acid (98 wt%) added to it 5 and stirred for 5 minutes at 24 °C, under 20 psi Ar in an autoclave. The phases were separated. The oil phase was washed with 100 ml water. Washing is the thorough mixing and separation of the two phases. The oil phase was further washed (mixed) with 25 ml formic acid (96 wt%), formed two phases, and the phases separated. The oil phase was oxidized with 2.522 ml hydrogen peroxide (35 wt%) plus 36.6 ml formic acid (96 wt%) at 90 °C for 30 10 minutes in an autoclave. Two phases formed and were separated, the oil phase was washed with 100 ml water, separated and distilled. The distillation results are as follows: 59% of the total volume contained 15 ppm sulfur, 93% of the total volume contained 39 ppm sulfur, and 99% of the total volume contained 52 ppm sulfur. Table VI compares the sulfur content of the feed, the sulfuric acid treated feed, and the final oxidized gasoline product. Only 44 ppm 15 sulfur remained in the total product. The sulfur content of the gasoline in the boiling range of gasoline was substantially reduced to only 18 ppm sulfur. The total hydrocarbon content in the gasoline boiling range was not changed.

Table VI Catalytic Gas Series

(Selected Sulfur Balance, ppm S)

	Thio- phene	Methyl Thiophene	Tetra- hydrothiophene	Dimethyl- thiophene	Benzo- thiophene	Methyl Benzo- thiophene	Total Sulfur PPM	Total Sulfur ppm before 221 °C	Total Sulfur ppm before 221 °C	Total % Hydrocarbon before 221 °C
Feed	7	16	1	12	13	28	310	63	97	97
H₂SO₄	7				13	28	932	10	96	96
Product	2				13	13	246	18	97	97

EXAMPLE 7

[46] To demonstrate the effect of no diene pre-treatment on a high sulfur gasoline prior to oxidation, a gasoline containing 204 ppm sulfur was oxidized in two stages. In stage 5 1, 250 ml of gasoline (173 ppm sulfur) was oxidized with 1.74 ml hydrogen peroxide (35 wt%) and 25.3 ml formic acid (96 wt%) for 30 min at 90 °C in autoclave. In stage 2, the first stage product was further oxidized with 1.74 ml of hydrogen peroxide (35 wt%) and 25.3 ml of formic acid (96 wt%) for 30 min at 90 °C in autoclave. The resulting product had mercaptans and sulfides removed. No thiophenic compounds oxidized. Therefore, a feed 10 having a large amount of dienes was not sufficiently desulfurized by the oxidizing solution because the dienes more readily reacted with the oxidizing solution than the sulfur compounds.

EXAMPLE 8

[47] To demonstrate the effect of diene pre-treatment on a high sulfur gasoline 15 prior to oxidation, 250 ml normal high sulfur gasoline, see Example 7, was pretreated with 0.5 vol% (1.25 ml) sulfuric acid (98 wt%) at 18 °C for 5 minutes. The phases were separated by decanting. The oil phase was washed with 100 ml water, separated, and washed with 15 ml formic acid (96 wt%) and separated. The oil phase was then oxidized with 1.393 ml hydrogen peroxide (35 wt%) plus 20.2 ml formic acid (96 wt%) at 90 °C for 30 minutes in an 20 autoclave. The oxidized reaction product contained only 42 ppm S in the gasoline boiling range. The general hydrocarbon content remained unchanged.

EXAMPLE 9

[48] To demonstrate the effect of diene pre-treatment on a high sulfur gasoline prior to oxidation, 250 ml of normal high sulfur gasoline, see Example 7, was pretreated with 25 1.0 vol% (1.25 ml) sulfuric acid (98 wt%) at 18 °C for 5 minutes. The phases were decanted. The oil phase was washed with 100 ml water, separated, washed with 15 ml formic acid (96 wt%) and separated. Washing mixes the solution before allowing the phases to settle. The oil phase was oxidized with 1.393 ml hydrogen peroxide (35 wt%) plus 20.2 ml formic acid (96 wt%) at 90 °C for 30 minutes in an autoclave. The oxidized reaction product contained only 30 17 ppm S in the gasoline boiling range. The larger amount of sulfuric acid pre-treatment

reacted more dienes, enabling the oxidative desulfurization reactions. The general hydrocarbon content remained unchanged.

EXAMPLE 10

5 [49] To demonstrate the effect of no diene pre-treatment on commercial diesel, the sulfur in 250 ml of commercial diesel (331 ppm S, 102 ppm N) was oxidized with 2.961 ml hydrogen peroxide (35 wt%) plus 43.4 ml formic acid (96 wt%) at 95 °C for 30 minutes, in a glass flask reactor, and stirred. Eight times the stoichiometric level of oxidant was used. The resulting product was completely oxidized. Only 36 ppm sulfur remained below the boiling range of 356 °C. The remaining sulfur content was above 356 °C.

10

EXAMPLE 11

15 [50] To demonstrate the effect of diene pre-treatment on commercial diesel prior to oxidation, 250 ml diesel, see Example 10, (331 ppm S, 102 ppm N) was contacted with 5 ml (2 vol%) sulfuric acid (96 wt%) for 5 minutes at ambient temperature in glass flask reactor, and stirred. The phases were allowed to settle and were separated. The oil phase was washed with 100 ml water, separated, and washed with 20 ml formic acid (96 wt%). The sulfur in the oil phase was oxidized with 1.611 ml hydrogen peroxide (35 wt%) plus 21.7 ml formic acid (96 wt%) at 90-92 °C for 30 minutes in glass flask reactor, and stirred. Only 2.5 times the stoichiometric level of oxidant was used as compared to 8 times the stoichiometric level in Example 10. The resulting product was completely oxidized. Only 9 ppm sulfur remained in the hydrocarbon having a boiling point of below 356 °C. The remaining sulfur content was in the fraction boiling above 356 °C. In other words, without sulfuric acid pre-treatment, a little over 3 times the amount of oxidant was required to give a comparable low sulfur product.

20

EXAMPLE 12

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[51] To demonstrate the range of sulfuric acid for diene pre-treatment prior to oxidation, CAT gasoline (see Example 5) was pretreated with varying acid concentrations, percentages of acid volume, acid contact times and treatment temperatures. The pretreated CAT gasoline was oxidatively desulfurized to demonstrate the effectiveness of the pre-treatment. The sulfuric acid concentrations were varied from about 75 wt% to about 98 wt%.
30 The acid volume percentages were varied from about 0.5 to about 3 percent. The contact

time was varied from about 2 to about 15 minutes. The contact temperature was varied from about 25 to about 60 °C. See Table VII. Lower concentrations of sulfuric acid did not remove interferences to oxidative desulfurization and the sulfur oxidation failed. The sulfuric acid concentrations of 93% and 98% provided acceptable desulfurization. The higher the 5 percentage of acid, the better the results were. By varying the contact time, five minutes provided the best results. The temperatures of 50 °C and 60 °C provided acceptable desulfurization results. The samples were oxidized in an 85 °C stirred autoclave for approximately 20 minutes using a formic acid to hydrogen peroxide molar ratio of about 30. In Table VII, 2x is 2 times the stoichiometric requirement (based on the original feed sulfur). 10 2x + 2x is a 2 stage process with 2 times the stoichiometric requirement in each stage. Total sulfur is the total sulfur after oxidation and is used to calculate the percentage of sulfur in the gasoline range (last column). The projected sulfur in the distillation product is from the interpretation of the GC/SCD chromatograms of the total sulfur relative to the hydrocarbon chromatograms.

Table VII Catalytic Gasoline Sulfuric Acid Treatments
Varying Sulfuric Acid Concentrations, Contact Times, Temperatures and Oxidant Amounts

H ₂ SO ₄ Concentration	percent acid volume	contact time	temperature °C	relative amount of oxidant	total sulfur	%S in gasoline	PPM in gasoline	gasoline range
not acid treated					404	83.3	337	
75	2	10	60	2x	364	59.0	215	
98	0.5	10	60	2x	397	37.2	148	
98	2	2	24 ~ 36	2x	452	16.6	75	
93	2	2	25	4x	374	19.6	73	
93	2	5	50	2x	401	18.4	74	
93	2	5	50	2x + 2x	398	15.2	60	
98	2	5	40	2x	458	16.6	76	
98	2	5	40	2x + 2x	382	15.6	60	
93	2	15	40 ~ 56	2x	448	17.4	78	
93	2	15	40 ~ 56	2x + 2x	411	12.8	53	
93	2	5	50	x	458	16.6	76	
93	2	5	50	x + x	440	9.8	43	
93	3	5	50	2x	506	13.4	68	
93	3	5	50	2x + 2x	440	9.4	41	

EXAMPLE 13

[52] To demonstrate the effect of recycling the pre-treatment acid on subsequent oxidation processes, a sample of CAT gasoline was pretreated with 93% sulfuric acid at 50 °C for 5 minutes in three steps. The first step contacted the CAT gasoline with 2 vol% fresh 5 sulfuric acid. In the second step, without removing the original amount of sulfuric acid, an additional 1 vol% of fresh acid was contacted with the product of the first step. In the third step, without removing the sulfuric acid from the second step, an additional 0.5 vol% fresh acid was contacted with the product from the second step.

[53] After each step, a sample was removed and oxidized. The difference in the 10 oxidation product between the second step and the third step are minimal. Some recycle of the pre-treatment acid increases the sulfur removal by oxidation, but there was a limit before the sulfur amount actually increases. In Table VIII, x is the stoichiometric requirement (based on the original feed sulfur). x + x is a 2 stage process with the stoichiometric requirement in each stage. Total sulfur was the total sulfur after oxidation and was used to calculate the 15 percentage of sulfur in the gasoline boiling range (last column). The projected sulfur in the distillation product was from the interpretation of the GC/SCD chromatograms of the total sulfur relative to the hydrocarbon chromatograms.

Table VIII Catalytic Gasoline Sulfuric Acid Treatments Recycling Sulfuric Acid

pre-treater acid volume	relative amount of oxidant	total sulfur	%S in gasoline range	PPM S
		282	37.8	107
2 fresh	x	743	37.7	280
	x + x	550	14.8	81
2 recycled +1 fresh	x	729	10.1	74
	x + x	388	7.6	29
3 recycled + .5 fresh	x	656	11.1	73
	x + x	356	9.2	33

EXAMPLE 14

[54] To demonstrate oxidation and distillation of sulfuric acid treated gasoline, a CAT gasoline containing 412 ppm sulfur was pretreated with a 2 vol% sulfuric acid. The organic phase was separated and water washed. The resulting sulfuric acid treated product 5 contained 3126 ppm sulfur. The sulfur content was distributed between thiophenic species that are naturally found in gasoline fuels, plus alkyl sulfate addition products that were newly formed during the acid treatment. 250 ml of the water washed-sulfuric acid treated gasoline was then oxidized in two stages. During the first stage, the gasoline was oxidized with 1.4 ml hydrogen peroxide (35%) plus 13.6 ml of formic acid at 85 °C for 20 minutes in an autoclave.

10 The partially oxidized gasoline was further oxidized with 2.3 ml of hydrogen peroxide and 22.7 ml of formic acid at 85 C for 20 minutes in an autoclave. After water washing the resulting oxidized gasoline contained 1262 ppm sulfur. The final oxidized gasoline was distilled to remove the heavy sulfated species, which have boiling products above the distillation range of gasoline. The sulfur content of the distilled gasoline was 114 ppm sulfur.

15 However, some sulfur trioxide was released by the decomposition of alkyl sulfate during distillation and contributed to the total sulfur value of 114 ppm. This was removed by water washing, resulting in a final washed distilled product having a sulfur level of 43 ppm, see Table IX. As an alternative, contacting with lime yields approximately the same product.

The six cuts are combined to create the final gasoline product.

20

TABLE IX Distillation of Presulfated Oxidized Gasoline

Cut	<°C	mass	PPM S	
			no wash	water wash
1	133	24.8	5	4
2	189	29.4	8	8
3	204	9.1	35	22
4	258	33.2	262	100
5	266	4.0	479	203
6	268	<u>1.3</u>	<u>262</u>	<u>231</u>
		101.8	114	43

[55] The foregoing description of the invention and the embodiments of the specific examples described demonstrate the features of pretreating a sulfur containing hydrocarbon fuel with sulfuric acid prior to a process for desulfurizing the hydrocarbon fuels. The above-described description is offered for purposes of disclosing the features of the 5 instant invention for use in desulfurizing the aforementioned fuel oils. Having been taught such process by the above discussion and examples, one of ordinary skill in the art could make modifications and adaptations to such process without departing from the scope of the claims appended hereto. Accordingly, such modification, variations and adaptations of the above-described process and compositions are to be construed within the intended scope of 10 the claims which follow.

[56] What is claimed is: